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On the magnetism of liquid nitrogen–liquid oxygen mixture

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Abstract

The measurements of EPR line width in liquid nitrogen–liquid oxygen mixtures are presented. The observed anomalous dependence of line width on oxygen concentration can be understood if the existence of O_2–O_2–O_2 and N_2–O_2–O_2 molecular clusters is assumed. The provided quantum chemical calculations give the spatial structure as well as the bond energy for these clusters.

Keywords: Liquid oxygen; Liquid nitrogen; Electron paramagnetic resonance

In spite of the properties of liquid oxygen being the subject of investigations by various methods for almost one hundred years, the structure of liquid oxygen is not yet understood completely. The possibilities for some short-range order existence in liquid oxygen were discussed, for example, in Ref. [1] (neutron diffraction measurements) and in Ref. [2] (heat and magnetic measurements near melting point). The additional information about such a short-range order can be obtained from electron paramagnetic resonance (EPR) measurements. Usually EPR line width is decreased with the lowering of paramagnetic centers concentration. However, a rather strong increasing of the EPR line width of paramagnetic oxygen molecules was found [3] at oxygen concentration close to zero. The reasons for such behavior were not investigated but it is clear that if some short-order exists in liquid oxygen, the additional contribution to EPR line width has to appear. In order to investigate this problem we have provided the EPR measurements in *liquid nitrogen–liquid oxygen* mixtures. Note that this experimental study was also interested in verifying the possibility of paramagnetic oxygen molecules use for the dynamic polarization of noble gas nuclei.

The results of our EPR measurements are summarized in Fig. 1. Note that EPR line width in *liquid nitrogen–liquid oxygen* mixture almost does not depend on the amount of O_2 molecules at 35–70 oxygen concentration. The observed anomalous increasing of the line width at smaller concentration can be explained by assuming the formation of different clusters in *liquid nitrogen–liquid oxygen* mixtures. These clusters may consist of diatomic diamagnetic N_2 and paramagnetic O_2 molecules. The positions and mutual orientations of molecules in clusters are fixed, so rather strong dipole–dipole interactions inside these clusters are not averaged by motion and the EPR line is wide. Moreover because of the lower mobility of clusters the additional contribution to the line width in comparison with a liquid containing only molecules can be expected due to dipole–dipole interaction between clusters.

The special quantum chemical calculations of electronic and spatial structure of possible clusters have been carried out by an ab initio method at the unrestricted Hartree-Fock self-consistent field (UHF-SCF) level of theory using a 6-31G(d) basis set. The influence of electron correlations was taken into account within the framework of the density functional theory (DFT) on the basis of the Beckes three-parameter hybrid method [4] employing the correlation functional [5] which includes both local and non-local terms. The geometry

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